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January 24, 1985

RECEIVED BY

JAN 29 1985

LEGAL DEPARTMENT
CAMBRIDGE, MAGeorge Dana Bisbee, Esquire
Attorney General's Office
State House Annex
Concord, New Hampshire 03301

Re: W.R. Grace -- Barrels at Rodgers Mobile Home Park Site

Dear Dana:

Enclosed is a summary of the analytical results from the Quality Control Laboratory at W.R. Grace's Nashua facility on thirty-five samples taken from drums of solid waste at the Rodgers Mobile Home Park site. Attachment 1 lists those drums sampled and the identification of the substances contained therein. Attachment 2 is a list of various tests used by the Nashua facility to identify the waste material. Some of these tests are standard while others have been developed by Grace. Attachment 3 consists of material safety data sheets for some of the identified Grace materials.

Of the thirty-five samples taken by Grace personnel from barrels at the site, thirty-one have been tentatively identified as Grace material. Similar materials are still produced as waste streams by the Nashua plant, and it is expected that with the possible exception of Drum #277 (NTA nitril), which may contain cyanide in trace amounts, all wastes would be classified as non-hazardous. None of the types of wastes identified are on any of the EPA or New Hampshire hazardous waste lists. We anticipate that any waste disposal contractor hired to remove the drums will do so after similar sampling of the materials contained in the drums. We will supply you with a proposal for sampling and drum removal procedures by the disposal contractor selected by Grace.

The thirty-five samples were from two different locations at the site. Those samples beginning with the number 2 are from the estimated three hundred solid waste drums staged and located near the former drummed liquid staging area. Those samples with the prefix A or D are from the crushed drum area at the far end of

George Dana Bisbee, Esquire
January 24, 1985
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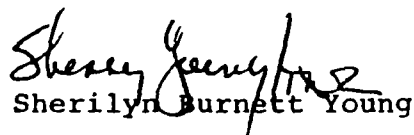
the landfill. Samples were taken from drums that had a Hampshire Chemical label or which contained wastes identified by the Nashua plant environmental coordinator as being similar in appearance to wastes commonly generated by the plant. For your information, the Nashua plant produces several types of products. Chelating agents and sarcosine surfactants and sarcosinates are the two major product lines. Chelating agents are chemical compounds used to modify the undesirable effects of hard water metallic impurities in textile processing, soap and detergent manufacture, photographic and other chemical processes, and to prevent scale formation in industrial uses of water. They are also used to supply soil deficient metals to plants and trees.

Sarcosine surfactants and sarcosinates (the sodium salt of N-methyl glycine) are used in the manufacture of personal care products, such as soaps, hair shampoos, dentifrices, shaving creams, and other products to improve foaming and cleansing properties. The EPA-listed volatile organic compounds are not used in the manufacture of either product line.

Once we have supplied you with a proposal from our selected waste disposal outfit, including a proposal for sampling and waste disposal procedures of the barrels located at the Rogers site, we will await your response to those submittals before committing to a final barrel removal action. We have had one waste disposal outfit at the site during the week of January 21 to assess the situation and prepare the proposals for sampling and disposal, and anticipate shortly having a second disposal outfit do the same. We hope to submit to you a proposal from our selected waste contractor by February 1, 1985.

Should you have any questions about the above-discussed matters, feel free to call me.

Very truly yours,


Sherilyn Burnett Young

SABY:mjb
Enclosure
c: Mark Stoler, Esquire
W.R. Grace

P.S. to Mr. Bisbee:

I have details regarding the laboratory procedures used for the tests devised by Grace to analyze its products. These procedures are proprietary and confidential, but limited access to same will be provided under controlled conditions if the State

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feels it is necessary to provide these for purposes of reviewing
the laboratory analyses undertaken by Grace.

SABY

F

ATTACHMENT 1

CHARACTERIZATION OF SAMPLES TAKEN AT THE RODGERS MOBILE HOME
PARK SITE BY GRACE PERSONNEL

DRUM NO.	Tentative Identification
D-1	Water insoluble layer from phosphoric acid byproduct from manufacture of fatty acid chlorides
D-3	"
A-1	"
A-5	"
A-6	"
A-10	"
259	"
260	"
275	"
283	"
286A	Filter paper used to filter 5% iron chelate product
286B	Insolubles filtered from 5% iron chelate product
277	NTA nitrile (nitrotriacetoneitrile)
284	EDTA byproduct (ethylenediamine tetraacetate or sodium salt of EDTA)
287	"
290	"
291	"
A-11	Fatty acid or fatty acid sarcosinate byproduct
266	"
270	"
273	"
274	"
278	"
278N	"

257	Spent charcoal (used to filter EDTA out of chelate solutions)
261	"
263	"
264	"
265	"
281	"
292	"

Samples from drums that have not been tentatively identified
as Grace material are:

243A	Contains ammonia and sulfate
267	Dirt
268	Unknown
269	Dried paint

ATTACHMENT 2

TESTS USED BY W.R. GRACE & CO. NASHUA PLANT QUALITY CONTROL LAB

1. Determination of Iron in Iron Chelates
2. Sulfate Content of Chelate Acid
3. Determination of Cyanide in NTANa
4. Trace Cyanide in Chelating Agents
5. Chelation Value
6. pH
7. Assay of Amines
8. Residue of Ignition
9. Chelation Value of NTA and its Salts
10. Determination of Total HCN in Wastewater by Technicon
11. Analysis of Chelating Agents by Silylation/Gas Chromatography
12. Solubility in Water (Cold)
13. Solubility in Water (Hot)
14. Solubility in HCL
15. Solubility in NaOH
16. Solubility in Ether
17. Solubility in Butyl Acetate
18. Odor
19. Flame Test
20. Test for NH₃ by addition of cold NaOH
21. Test for NH₃ by addition of hot NaOH

ORGANIC CHEMICALS DIVISION
HAMPSHIRE CHEMICAL
STANDARD ANALYTICAL PROCEDURE

Number: 0115F

Date: September 5, 1975

Determination of Iron in Iron Chelates

Principle of Method:

The sample is digested under strong oxidizing conditions to destroy organic matter. The iron in the digest is then determined chelometrically.

Reagents Required:

1. EDTA, 0.1 molar (see Standardization Procedure #27)
2. Oxidizing Acid (O-2)
3. Variamine Blue Indicator
4. Chloracetate Buffer (C-3)

Apparatus Required:

1. Kjehldahl Flask, 100 ml.
2. Gas Burner

Procedure:

A. Sample Preparation

Weigh accurately required sample size as shown in Table I into a 100 ml. digestion flask. Boil carefully to dryness. Add 5 ml. oxidizing acid. Boil gently to near dryness. Cool flask with air hose. Repeat digestion using 5 ml. of oxidizing acid. Cool sample. Add 40 ml. distilled water. Heat gently until clear solution is obtained. Transfer solution quantitatively to a 250 ml. beaker.

B. Titration

To the digested sample, add 25 ml. of chloracetate buffer. Adjust to pH 2.5-3.0 with ammonia or HCl. Heat to 60°C, add a pinch of Variamine Blue indicator and titrate to a clear yellow endpoint with 0.1 molar EDTA.

Calculation:

$$\text{Fe, \%} = \frac{(\text{mls. EDTA})(\text{molarity})(5.585)}{\text{sample weight in gms.}}$$

TABLE ISAMPLE WEIGHTS

<u>Nominal Iron Content, %</u>	<u>Sample Weight Required</u>
14	0.5 gm.
9	0.8 gm.
5-6	1.5 gm.
1 or less	10.0 gm.

Notes:

1. A face shield must be worn during acid digestions.
2. Samples of Ferric Ammonium EDTA must always be analyzed in duplicate.

THIS ISSUE SUPERSEDES SAP0115E DATED AUGUST 9, 1972.

RWK/smo

HAMPSHIRE CHEMICAL CORPORATION

Standard Analytical Procedure

Number 0063A

Date Issued: January 11, 1965

Sulfate Content of Chelate Acid

Principle of Method:

Qualitative test for $\text{SO}_4^{=}$ with Ba^{++} .

Reagents Required:

2% barium chloride: 2 g of BaCl_2 dissolved in 100 ml. of water.

Procedure:

A quantity of acid, approximately one-half of a 250 ml. beaker full, is slurried with distilled water and the slurry filtered through a suction funnel. To a portion of the filtered solution in a test tube some BaCl_2 solution is added. The product is considered essentially sulfate free if no more than a very faint haze develops in about 5 minutes.

HAMPSHIRE CHEMICAL DIVISION
OF
W. R. GRACE & CO.

Standard Analytical Procedure

Number: 0149

Date Issued: September 30, 1970

Name: Determination of Cyanide in NTANa_3

Principle of Method

Reduction of alkaline picrate solution by cyanide to form a colored complex which is measured colorimetrically at 540 m μ . To compensate for color enhancement by NTA and other non-cyanide interferences a replicate sample is heated with formaldehyde to destroy cyanide. The replicate sample is then used for preparation of reagent blank and calibration standard.

Reagents Required:

- 1) Picric Acid, 1% aqueous; dissolve 12 grams of picric acid crystals in 1000 ml. of hot distilled water. Cool and adjust to volume with distilled water.
- 2) Sodium Carbonate, 0.625 Molar; dissolve 66.25 grams of anhydrous Na_2CO_3 in sufficient distilled water to make one liter.
- 3) Sodium Cyanide Solution:
 - a) Weigh accurately 1.815 grams of sodium cyanide, granular, (DuPont Cyanogran) into a 500 ml. volumetric flask and dilute to volume with distilled water. Pipet a 50 ml. aliquot into a 250 ml. beaker and titrate with 0.1N AgNO_3 as described in SAP 0020. Calculate "K" (Mg HCN/ml) as follows:

$$K = \frac{(\text{ml } \text{AgNO}_3) (\text{normality})}{1082.0}$$

This is the cyanide stock solution.

- b) Pipet 25 ml. of stock solution into a 1000 ml. volumetric flask. Dilute to volume with distilled water. This is Solution A and contains 0.025K mg HCN/ml.
 - c) Pipet 25 ml. of Solution A into a 50 ml. volumetric flask and dilute to volume with distilled water. This is "Calibration" solution and contains 0.0125K mg HCN/ml.

These solutions must be prepared within three days of the date of use.

- 4) Silver Nitrate, 0.1N (see standardization method 3)

5) Formaldehyde Solution:

Weigh accurately about 12 grams of 37% CH_2O solution which has been assayed by SAP 0078, into a 100 ml. volumetric flask. Dilute to volume with distilled water. Use the proper aliquot of this solution to prepare a dilute formaldehyde solution (b) which must contain 0.684 g. CH_2 per liter.

6) Ammonium Chloride Solution:

Dissolve 0.975 g. NH_4Cl in sufficient distilled water to make one liter of solution.

Procedure

A) Preparation of Sample Stock Solution

Weigh $214 \pm$ g. of $\text{NTANa}_3 \cdot \text{H}_2\text{O}$ sample into 500 ml. flask and add distilled water to make 500 g. \pm 1 g. of solution.

B) Preparation of Sample Solution

Weigh 40.00 ± 0.01 g. of stock solution into a 100 ml. beaker and adjust to pH 10.5-10.7 with 1:1 HCl. Transfer to 100 ml. volumetric flask and dilute to volume.

C) Preparation of CH_2O - treated Sample Solution

Weigh 40.00 ± 0.01 g. of stock solution into a 4 ounce wide mouth jar. Add 1.0 ml. of formaldehyde solution, swirl to mix contents, and cover tightly with bakelite pulp + vinyl caps. Place in oven at 98°C for at least four (4) hours. Remove from oven and add 1.0 ml. of NH_4Cl solution while solution is still hot. Cool, adjust to pH 10.5-10.7 with HCl or 10% NaOH, transfer to 100 ml. volumetric flask and dilute to volume with distilled water.

D) Picric Acid Treatment

Into each of three 25 ml. volumetric flasks pipet 5 ml. of picric acid solution and 4 ml. of sodium carbonate solution. Label the flasks "Reagent Blank", "Calibration Standard", and "Sample". Pipet 5 ml. of sample solution into the "Sample" flask. Then pipet 5 ml. of CH_2O treated sample into each of the remaining flasks. To the "Calibration Standard" flask, pipet 1.0 ml. of HCN Calibration Solution. Swirl the Flasks.

E) Color Development

Place the unstoppered flasks in a steam bath for exactly 5 1/2 minutes. Remove quickly from steam bath and immediately place in an ice bath for several minutes. Dilute to volume with distilled water.

F) Colorimetry

Place samples in one-inch colorimetric cells and set colorimeter at 540 mm. With "reagent blank" in cell holder, balance colorimeter at zero absorbance. Then measure absorbance of "Sample" and "Calibration Standard".

G) Calculation

$$\begin{array}{l} \text{HCN, ppm} \\ \text{(Anhydrous NTANa}_3 \text{ basis)} \end{array} = \left(\frac{\text{absorbance of "Sample"}}{\text{absorbance of "Calibration Std"}} \right) (0.015625K)$$

ORGANIC CHEMICALS DIVISION
HAMPSHIRE CHEMICAL
STANDARD ANALYTICAL PROCEDURE

Number: SAP 0151B

Date: January 12, 1976

Trace Cyanide in Chelating Agents

Principle of Method:

Amperometric titration of CN^- radical with silver nitrate.

Apparatus:

1. Microammeter, 0-100 range, with platinum and silver electrodes.
2. Amber Buret, scientific glass #B8064, 500 ml., 5 ml., ± 0.01 scale div.

Reagents:

1. Silver nitrate, 0.001 Normal; dilute 10 ml. of 0.1000M silver nitrate to 1 l. Prepare daily.
2. Sodium sulfite, 1 Molar; dissolve 125 g. anhydrous Na_2SO_3 in water to make 1 l. Not standardized.
3. Silver nitrate, 0.01 Normal; dilute 100 ml. 0.1000N AgNO_3 to 1 l.

Procedure:

Weigh accurately appropriate sample size shown in Table I into 100 ml. beaker. Add 2 ml. 1 molar sodium sulfite, 1 ml. 50% NaOH, and water to make a total volume of about 80 ml. Immerse electrodes in solution, and titrate with appropriate AgNO_3 using microburet until current reading on ammeter is exactly zero.

Calculation:

$$\text{HCN, ppm} = \frac{(\text{ml. AgNO}_3)(\text{normality})(54100)}{\text{wt. sample in g.}}$$

Notes:

1. Rinse electrodes with distilled water before and after use.
2. Never immerse electrodes in strongly acid solution.
3. Do not leave electrodes immersed in any liquid when not in use.

TABLE I

<u>Nominal HCN, ppm</u>	<u>Sample Weight</u>	<u>AgNO₃ Normality</u>
<10	20	0.001
<100	20	0.01
200-300	10	0.01

THIS ISSUE SUPERSEDES SAP0151A DATED NOVEMBER 5, 1970.

RWK/smo

ORGANIC CHEMICALS DIVISION

W.R. Grace & Co.

STANDARD ANALYTICAL PROCEDURE

Number: 0001G

Date Issued: April 19, 1978

Chelation Value

Principle of Method:

Chelation of calcium ion by chelating agent in alkaline solution. Excess Ca^{++} ion added is noted by precipitation as calcium oxalate.

Reagents Required:

1. Calcium acetate solution (See Standardization Method No. 1)
2. Sodium oxalate solution (S-3)
3. Sodium hydroxide 50%
4. pH paper: high pH range

Procedure:

Weigh accurately the appropriate sample size as shown in sample size calculation and dissolve in approximately 85 ml. of distilled water. Adjust solution with 50% NaOH to a pH above 11, using pH test paper. Add 10 ml. of sodium oxalate solution. Titrate with calcium acetate solution to a distinct and permanent turbidity. Check pH with test paper. If pH above 11, this is the end point; if pH below 11, add a few drops of 50% NaOH and continue titration to permanent turbidity.

Calculations:

$$\text{Chelation Value} = \frac{\text{ml. Ca (OAc)}_2 \text{ solution} \times F}{\text{Weight of sample in grams}}$$

Where $F = \text{mg. CaCO}_3/\text{ml.}$

$$\% \text{ EDTA Na}_4 = (\text{chelation value}) (0.3798)$$

$$\% \text{ HEEDTANa}_3 = (\text{chelation value}) (0.3445)$$

$$\% \text{ HEDTA Acid} = (\text{chelation value}) (0.2779)$$

NOTE: Duplicate determinations must be run on Hampol 120; the mean value is then recorded as chelation value of the sample.

SAMPLE SIZE CALCULATION

$$\text{Required sample size in grams} = \frac{510}{\text{estimated chelation value}}$$

THIS ISSUE SUPERSEDES SAP No. 0001F DATED APRIL 4, 1973.

ORGANIC CHEMICALS DIVISION

W. R. Grace & Co.

STANDARD ANALYTICAL PROCEDURE

Number: 0002D

Date: January 17, 1979

pH of Solutions at 25°C

Principle of Method:

The pH of an aqueous solution, diluted to appropriate concentration is determined with an ORION pH meter.

Reagents Required:

Standard pH buffers: pH 2.00, pH 7.00, pH 10.00 prepared and used according to manufacturer's instructions.

Apparatus:

- 1) ORION Model 601 pH meter or equivalent.
- 2) ORION 91-05 combination electrode.

Procedures:

Adjust all samples to 25°C before measurement.

Method A (for routine measurements)

- 1) Turn slope indicator dial to 100% and turn temperature knob to 25°C.
- 2) Rinse off electrode with deionized water.
- 3) Place electrode in calibration buffer 7.00. Stir vigorously on magnetic stirrer and wait for a stable reading (about 30 seconds).
- 4) Set meter to pH 7.00 with the calibration control.
- 5) Remove electrode from buffer and rinse off with deionized water.
- 6) Place electrode in sample and stir vigorously for 30 seconds.
- 7) Stop stirring and read sample pH to the nearest 0.1 pH unit.

Method B (for precise measurements)

- 1) Place electrode in deionized water and stir water vigorously. Remove water droplets from electrode.

- 2) Place electrode in a pH 7.00 calibration buffer and stir vigorously. Stop stirring and wait for stable reading.
- 3) Set calibration control so that meter reads 7.00.
- 4) Rinse electrode with deionized water.
- 5) Select a pH 2.00 or a pH 10.00 calibration buffer, whichever is closest to sample pH and immerse electrodes in it while stirring. Stop stirring and wait for a stable reading.
- 6) Set meter reading to pH of the calibration buffer with the temperature compensator knob. Turn plastic slope indicator until arrow points to buffer temperature. The percent slope should be greater than 90%. If not, electrode may be dirty or may be defective. See cleaning procedure in Appendix II.
- 7) Remove electrode from buffer, rinse with deionized water. Then dry electrode with a wiper.
- 8) Place electrode in sample. Stir vigorously for at least 30 seconds. Stop stirring and wait for a stable reading. Read sample pH to the nearest 0.01 pH unit.

RWK/lmw
Att. (2)

THIS ISSUE SUPERSEDES SAP 0002C DATED NOVEMBER 18, 1971.

APPENDIX I

SAMPLE DILUTION PROCEDURE

All samples are diluted on a wt/volume basis.

Example 1: 1% solution.

Weigh 1.00 gram sample to the nearest 0.01 gram. Dissolve in deionized water and dilute to 100 ml. with deionized water. Adjust temperature to 25°C.

Example 2: Saturated solution of chelating agent

Slurry 5.0 grams of solids with 95 ml. deionized water. Heat on a steam bath for 10 minutes and then cool to 25°C.

RWK/lmw
1/19/79

APPENDIX IIELECTRODE CLEANING PROCEDURE

For 5 minutes,

- 1) Immerse electrode tip only in a 38% solution of $\text{Na}_3\text{PO}_4 \cdot 12 \text{H}_2\text{O}$ that has been heated to 50°C . Rinse and repeat this procedure.
- 2) Perform calibration Method B.
- 3) If electrode slope is less than 90%, replace electrode.

RWK/lmw
1/19/79

ORGANIC CHEMICALS DIVISION

W.R. Grace & Co.

STANDARD ANALYTICAL PROCEDURE

Number: 0011E

Date: June 6, 1978

Assay of Amines

Principle of Method:

Non-aqueous titration suitable for compounds which exhibit weakly alkaline dissociation.

Reagents Required:

1. Perchloric Acid, 0.1 normal for equivalent weight determination; see Standardization Method No. 44.
2. glacial acetic acid.
3. acetonitrile, reagent grade
4. Crystal Violet Indicator, 0.1% in acetic acid (C-5).

Apparatus Required:

1. Buret, straight, 25 ml. capacity, Class A.

Procedure:

1. Add 3-4 drops crystal violet indicator to about 60 ml. glacial acetic acid. Add 0.1N HClO_4 dropwise until solution is emerald green. This is neutralized acetic acid.
2. Weigh accurately the required amount of sample specified in Table 1 into a 150 ml. beaker. Use a disposable syringe for volatile samples.
3. Add 50 ml. neutralized acetic acid and 10 ml. acetonitrile if required in Table 1.
4. Heat sample gently on a hot plate until solution is effected. Cool to room temperature and add 5-6 drops crystal violet indicator.
5. Titrate with 0.1N HClO_4 to an emerald green endpoint.

Calculation:

$$\text{Assay, \%} = \frac{(\text{mls. HClO}_4)(\text{normality})(\text{Factor})}{\text{weight sample in grams}}$$

Reference:

Union Carbide Chemicals Co. Works Laboratory Manual 1, EA Method 31-7-3
April 13, 1956.

RWK/lmw

TABLE 1

<u>Code No.</u>	<u>Compound</u>	<u>sample weight, grams</u>	<u>Factor</u>	<u>Solvent System</u>
0830	glycine	0.15-0.30	7.51	A
1020	aminoethyldiethylamine	0.12-0.23	5.81	A
1040	Diethanolamine	0.21-0.42	10.51	A
1010	Diethylenetriamine	0.07-0.14	3.45	B
1000	ethylenediamine	0.06-0.12	3.01	B
1030	triethanolamine	0.30-0.60	14.92	A
1050	monoethanolamine	0.12-0.24	6.11	A

Solvent Systems:

A: 50 ml. glacial acetic acid only

B: 50 ml. glacial acetic acid plus 10 ml. acetonitrile.

RWK/lmw
6/8/78

DEWEY AND ALMY CHEMICAL DIVISION

HAMPSHIRE CHEMICAL

Standard Analytical Procedure

Number: 0050B

Date: October 12, 1972

Residue on Ignition

Principle of Method

Ignition of organic matter

Procedure:

Weigh accurately 5.000 grams of sample into a previously ignited tared ^{Pt}~~silica~~ crucible. Carefully ignite at low temperature until thoroughly charred. Place a ceramic chimney over the crucible and ignite the residue using a Meker burner until all carbon is volatilized. Cool in dessicator and weigh the residue.

$$\% \text{ Residue} = \frac{\text{weight residue in grams} \times 100}{\text{weight sample in grams}}$$

NOTE:

If SAP 0031 and/or SAP 0162 is required on the sample, the residue obtained may be used for further analyses.

THIS ISSUE SUPERSEDES SAP 0050A DATED SEPTEMBER 1, 1967

DEWEY AND ARMY CHEMICAL DIVISION

HAMPSHIRE CHEMICAL

Standard Analytical Procedure

Number: 0041D

Date Issued: June 27, 1974

Chelation Value of NTA and its Salts

Assay of NTA and its Salts

Principle of Method:

Chelation of copper in a solution buffered at pH 5.5-6.0 with hexamine.

Reagents Required:

1. Cupric chloride, 0.1 molar (see standardization method 13)
2. Hexamine Buffer - Dissolve 200 g. hexamethylene tetramine in 800 ml. water. Adjust to pH 6.0 with conc. HCl. Add 0.06 g. of Chromazurol S and dissolve.

Procedure:

Weigh accurately about 0.5 g. of solid or 0.6 g. of solution into a tared 250 ml. beaker. Add 50-75 ml. of water and 25 ml. of hexamine buffer. Titrate with 0.1M CuCl₂ to a sharp color change from green to blue. Be sure that solution is at pH 6.0 at the endpoint. See Table 1 for appropriate constant.

Calculation:

$$\% \text{ NTA derivative} = \frac{(\text{ml. CuCl}_2)(\text{molarity})(K \text{ factor})}{\text{sample weight in grams}}$$

$$\text{Chelation Value} = \frac{(\text{ml. CuCl}_2)(\text{CV factor})}{\text{sample weight in grams}}$$

TABLE 1

<u>NTA Derivative</u>	<u>K Factor</u>
NTA acid	19.11
NTA Na ₂	23.51
NTA Na ₂ ·2H ₂ O	25.31
NTA Na ₃	25.71
NTA Na ₃ ·H ₂ O	27.51

THIS ISSUE SUPERSEDES SAP0041B DATED OCTOBER 1, 1970.

RWK/smo

ORGANIC CHEMICALS DIVISION

W. R. Grace & Co.

EFFLUENT TREATMENT ANALYTICAL PROCEDURE

Number: 0023B

Date: April 24, 1981

Determination of Total HCN in Wastewater by Technicon
Autoanalyzer II

Reagents Required:

1. Distillation Reagent:

- a. Phosphoric Acid, 85% (H_3PO_4)(100 ml.);
- b. Distilled Water, q.s. (900 ml.);

Carefully add 100 ml. 85% phosphoric acid to 700 ml. distilled water and dilute to 1 liter with distilled water.

2. Phosphate Buffer, pH 5.2:

- a. Potassium Dihydrogen Phosphate (KH_2PO_4)(13.6 g.);
- b. Disodium Hydrogen Phosphate (Na_2HPO_4)(0.28 g.);
- c. Distilled Water, q.s. (1000 ml.);
- d. Brij-35* (Technicon #T21-0110) (0.5 ml.);

Dissolve 13.6 g. potassium dihydrogen phosphate and 0.38 g. disodium phosphate in 900 ml. distilled water and dilute to 1 liter. Add 0.5 ml. Brij-35 & mix.

3. Chloramine-T:

- a. Chloramine-T** ($\text{C}_7\text{H}_7\text{ClNO}_2\text{SNa} \cdot 3\text{H}_2\text{O}$) (2.0 g.);
- b. Distilled Water (500 ml.);

Dissolve 2.0 g. chloramine-T in 500 ml. distilled water.

4. Pyridine Barbituric Acid Reagent:

- a. Barbituric Acid*** ($\text{C}_4\text{H}_4\text{N}_2\text{O}_3$)(15 g.);
- b. Pyridine ($\text{C}_5\text{H}_5\text{N}$) (75 ml.);

* Trademark of Atlas Chemical Industries, Inc.

** Available from Eastman Kodak #1022.

*** Am. Drug & Chem. Co. 7901 San Fernando Rd., Sun Valley, CA 91352,
Tel. 213-768-4144.

c. Hydrochloric Acid, conc. (HCl)(15 ml.);

d. Distilled Water, q.s. (1000 ml.);

Prepare 15 g. barbituric acid in 1 liter beaker and add enough water (~100 ml.) to wash the sides of the beaker and wet the barbituric acid. Add 75 ml. pyridine and mix. Add 15 ml. HCl (sp.gr. 1.19) and mix. Dilute to ~900 ml. with distilled water and mix until all the barbituric acid has dissolved. Transfer the solution to 1 liter flask and dilute to volume with distilled water.

5. Potassium Ferrocyanide

Calibration Standard, 0.60 mg/liter as HCN

Prepare weekly as described in Appendix I, using reagent grade $K_4Fe(CN)_6 \cdot 3H_2O$, J. T. Baker Catalog No. 1-3114.

Procedure:

1.00 Set up the Technicon Autoanalyzer II using the cyanide chemistry module shown in figure 1.

2.00 Sample Preparation:

2.10 Liquid samples: Adjust to pH 6.5-7.5 with concentrated (85%) phosphoric acid. Dilute adjusted sample with DWAT so that nominal HCN concentration of resulting solution is between 0.1-1.0 mg/liter. If appreciable suspended solids are present, filter solution before analysis.

2.20 Solid Samples:

Weigh accurately 1.0 grams sample into a 100 ml. beaker containing about 70 ml. deionized water. Add concentrated HCl dropwise until pH of mixture is 6.5-7.5. Transfer to 100 ml. volumetric flask and dilute to volume.

2.21 If necessary, further dilute adjusted sample so that the nominal HCN concentration is between 0.1-1.0 mg/liter. If appreciable suspended solids are present, filter solution before analysis.

2.30 Analysis:

Introduce calibration standard and diluted sample solution to the analyzer and compare the peak height of the standard and samples, using the protocol described in the operation manual for the Autoanalyzer II. Multiply the results obtained by the appropriate dilution factor.

NOTES:

1. Set temperature of the heating batch at 150°C.

2. Flow rate of cooling water through the distillation apparatus should be ~750 ml./min. at ~14°C. See Instruction Manual TAI-0213-00 for operation of the distillation head.
3. Discard all calibration standards 7 days after preparation.

RWK/lmw
Attachments

THIS ISSUE SUPERSEDES EP 0023 DATED MAY 24, 1979.

Reason for change: Add sample preparation methods to procedure section.

Disk #3, file #5

APPENDIX I

PREPARATION OF POTASSIUM FERROCYANIDE CALIBRATION STANDARD
FOR AUTOANALYZER

1. Stock Solution A (600 mg/liter as HCN)

Weigh accurately 1.3187 grams Potassium Ferrocyanide into a 250 ml. beaker. Add 100 ml. deionized water and 2.0 grams of 50% reagent grade NaOH. Stir to dissolve and then transfer quantitatively to a one-liter volumetric flask. Dilute to volume with deionized water.

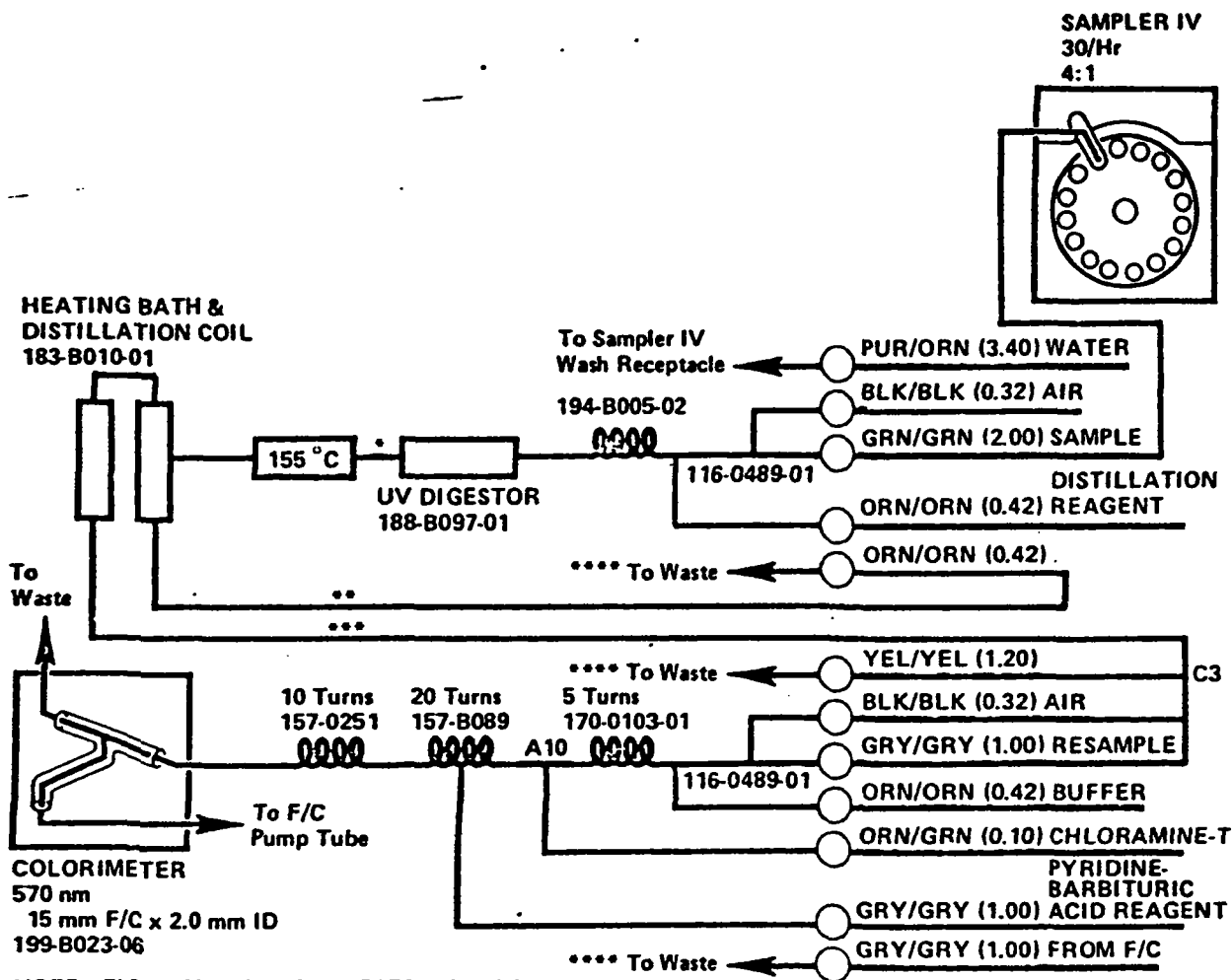
2. Stock Solution B (60 ml./liter as HCN)

Pipet 50 ml. of Stock Solution B into a 500 ml. volumetric flask and dilute to volume with deionized water.

3. Calibration Standard (60 mg/liter as HCN)

Using a 25 ml. straight buret, deliver 10.00 ml. of Stock Solution B into a one-liter volumetric flask. Dilute to volume. Prepare immediately before use.

RWK/lmw
5/24/79



NOTE: FIGURES IN PARENTHESES SIGNIFY FLOW RATES IN ML/MIN.

• 0.050 KEL-F[†] (562-3014-01)

•• 0.100 ACIDFLEX (116-0538-17)

••• 0.034 POLYETHYLENE (562-2004-01)

•••• SEE OPERATING NOTE 8.

[†] TRADEMARK OF 3-M COMPANY.

ORGANIC CHEMICALS DIVISION

W. R. Grace & Co.

Research and Development Standard Analytical Procedure

Number: 0022

Date Issued: October 1, 1979

Supersedes: SLIP GC-011-B

Title: Analysis of Chelating Agents by Silylation/Gas Chromatography

Written by: Wayne M. Coleman

Date: Sept. 17, 1979

Approved by:

John C. Thibault

Date: Oct. 1, 1979

Checked by:

Date:

Principle of Method

The sample components of chelating agents are derivatized to TMS esters and analyzed by gas chromatography.

Equipment Required

Instruments: Perkin-Elmer model No. 900 gas chromatograph equipped with temperature programming and a flame-ionization detector.
Perkin-Elmer Sigma-10 Data Processor or equivalent.

Column: 2' x 1/8" o.d. nickel tubing, packed with 10% DEXSIL 400 on Chromosorb WHP 100/120 mesh

Syringe: Unimetrics, 5 *μ*l capacity, equipped with a 2" needle

Septum vials, glass, 5 ml capacity with rubber stoppers

Savant Model No. SVC-100 Speed-Vac-Concentrator

Kontes Sample heater

Vacuum pump

Reagents Required

MSTFA silylating reagent (Pierce Chemical)
1:1 hydrochloric acid
Thymol blue indicator solution

Instrument Conditions

Column temperature: temperature programmed; one minute @ 90°C, then programmed @ 24°C/min from 90°C to 300°C.
Detector temperature: 315°C
Injector temperature: 275°C
Flow-rate: Helium @ 60 ml/min.
Injection volume: 2.0 μ l
Data Processor: Method #3

Procedure A: Blank

Inject 2.0 μ l of MSTFA silylating reagent into the gas chromatograph utilizing the conditions listed above. This reagent, when chromatographed, has been observed to give a small peak at the same retention time as glycolic acid. The peak may vary between batch lots; therefore, it is necessary to use the same lot when analyzing a set of samples. Any peak areas found by chromatographing the blank can be subtracted from the areas of component peaks found when running the sample.

Procedure B: Sample preparation

1. For Dry samples in the acid form

Weigh 20 mgs into a 5 ml septum vial and add by syringe 0.6 ml of MSTFA reagent. Stopper the vial immediately and shake well. Place the vial into the Kontes sample heater @ 60°C for 10 minutes with intermittent shaking. At this point the sample should be in solution and can be injected into the gas chromatograph as in Procedure A.

2. For Sodium Salt solutions of chelates containing NH and OH groups (e.g., HEDTA, DEG, IDA).

To a 5 ml septum vial, add 4 drops of sample solution, 10 drops of dist. water and 2 drops of Thymol-blue indicator. Add, by syringe, 1:1 HCl to a red color. Place the vial into the Speed-Vac-Concentrator and switch on the centrifuge. Do not use heat lamps when drying since glycolic acid will be lost. Turn on vacuum until the sample is dry. Remove from the concentrator and, using a micro-spatula, mix the sample to ensure that a crust does not form. Place the vial back into the concentrator for further drying. When thoroughly dry, proceed as in Procedure B#1.

Note a. If the sample contains a large quantity of glycolic acid, the dried material may appear syrupy.

- b. After derivatization, a layer of NaCl will be on the bottom of the vial. Inject portions of the upper clear layer only.

3. For Sodium Salt solutions of chelates containing only carboxyl groups (e.g., EDTA and NTA).
To a 5 ml septum vial, add 4 drops of sample solution and 4 drops of 1:1 HCl.
Proceed as in Procedure B #2.

Calculations

Subtract any interfering peak areas found in the blank and total all peaks in the sample.

$$\% \text{ of component in the mixture} = \frac{\text{area of component} \times 100}{\text{total peak areas}}$$

Response Factors

Synthetic mixtures may be made from pure components to obtain relative response factors if needed.

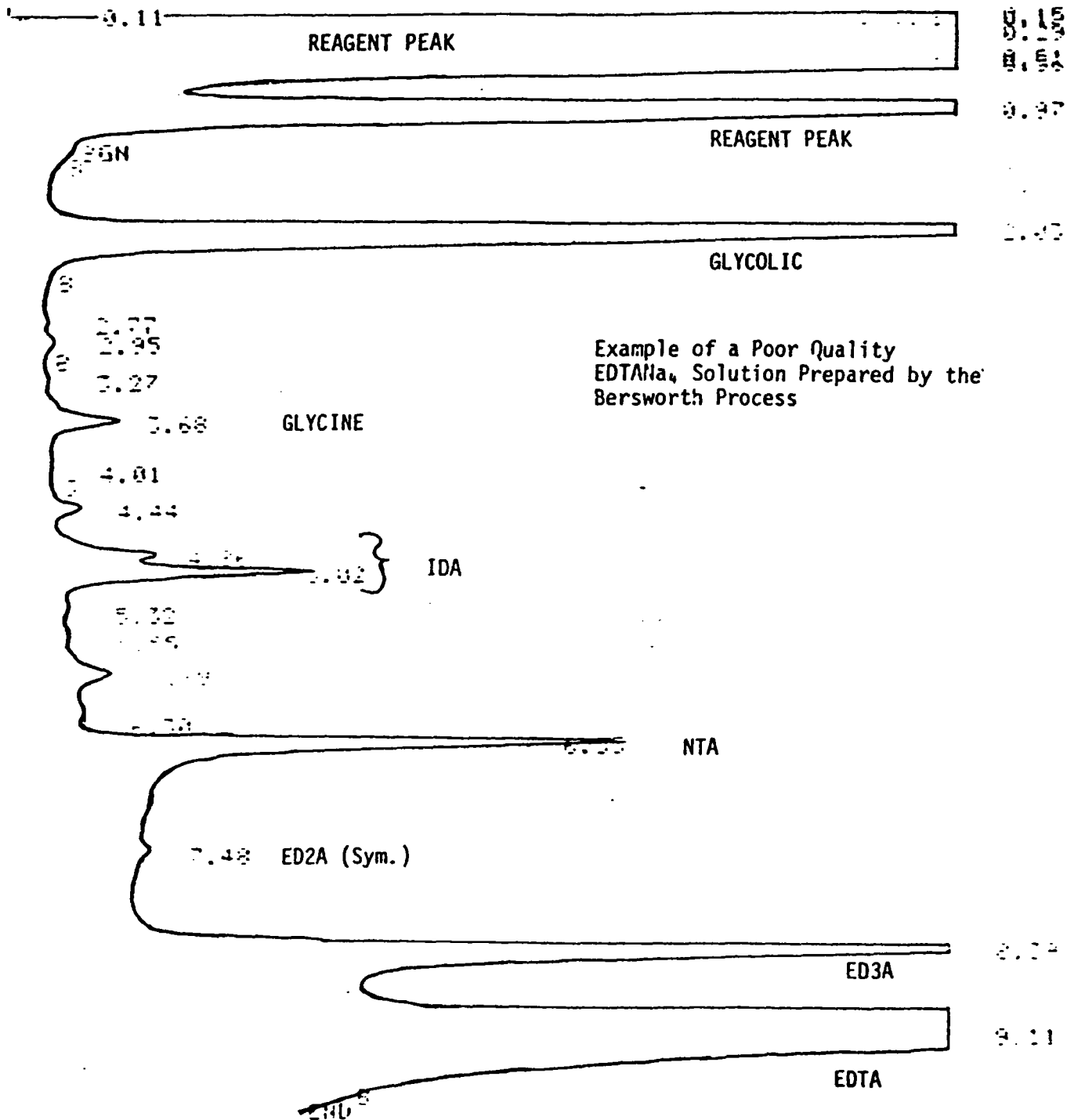
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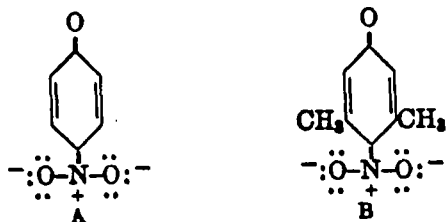
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ring. Such coplanarity is inhibited by the presence of the methyl groups in the ion (B).



A SURVEY OF THE SOLUBILITY CLASSES

Solubility in Water. Since water is a polar compound it is a poor solvent for hydrocarbons. Olefinic and acetylenic linkages or benzenoid structures do not affect the polarity greatly. Hence, unsaturated or aromatic hydrocarbons are not very different from the paraffins in their water solubility. The introduction of halogen atoms does not alter the polarity appreciably. It does increase the molecular weight, and, for this reason, the water solubility always falls off. On the other hand salts are extremely polar, the ones encountered in this work generally being water soluble.

Other compounds lie between these two extremes. Here are found the alcohols, esters, ethers, acids, amines, nitriles, amides, ketones, and aldehydes—to mention a few of the classes of frequent occurrence.

As might be expected, acids and amines generally are more soluble than neutral compounds. The amines probably owe their abnormally high solubility to their tendency to form hydrogen-bonded complexes with water molecules. This explanation is in harmony with the fact that the solubility of amines diminishes as the basicity decreases. It also explains the observation that many tertiary amines are more soluble in cold than in hot water. Apparently at lower temperatures the solubility of the hydrate is involved, whereas at higher temperatures the hydrate is unstable and the solubility measured is that of the free amine.

Monofunctional ethers, esters, ketones, aldehydes, alcohols, nitriles, amides, acids, and amines may be considered together with respect to water solubility. *In most homologous series of this type the upper limit of water solubility will be found in the neighborhood of the member containing five carbon atoms.*

This rule follows from a very general principle, that increased structural similarity between the solute and the solvent is accompanied by increased solubility. Because of the polar nature of water, compounds owe their solubility in it almost entirely to the polar groups which they may contain. As an homologous series is ascended, the hydrocarbon (non-polar) part of the molecule continually increases while the polar function remains essentially unchanged. There follows, then, a trend toward a decrease in the solubility in polar solvents such as water.

That the upper limits of water solubility for many series lie in the same neighborhood is due to the fact that the polarities of many functional groups are similar. The particular region (that of the member containing five carbon atoms) in these several series at which the upper limit of water solubility is reached is determined wholly by the altogether arbitrary proportions of solvent and solute chosen for use in this scheme of separation. It would have been equally easy and perhaps as satisfactory to employ a ratio of solute to solvent which would place the limit elsewhere.

The tendency of certain oxygen-containing compounds to form hydrates also contributes to water solubility. The stability of these hydrates is, therefore, a factor in determining water and ether solubility. Such compounds as chloral probably owe their great solubility in water to hydrate formation.

Low-molecular-weight esters of formic and pyruvic acids are hydrolyzed by water at room temperature as indicated by the fact that the aqueous solution becomes distinctly acid to litmus. They dissolve in ether without reaction and are placed in Class S₁.

Solubility in Ether. Whether a water-soluble compound will dissolve in ether depends on the nature and number of the functional groups. The presence of highly polar groups causes the compound to be very insoluble in ether; salts of amines and of organic acids do not dissolve.

Among non-ionic compounds, those that contain only one functional group are soluble in ether. Compounds containing more than one functional group generally show decreased solubility in ether (and increased solubility in water).

This is a corollary of the generalization concerning the limit of water solubility, for here the hydrocarbon (non-polar) portion of the molecule is kept nearly unchanged and the polar part is

multiplied. Ether is essentially a non-polar solvent, approaching the hydrocarbons in its physical properties. Consequently, a change that decreases the ratio of the hydrocarbon portion to the polar portion of the solute will decrease ether solubility. The decrease in solubility in non-polar solvents such as ether is, of course, attended by a corresponding increase in solubility in polar solvents such as water.

In case of doubt concerning solubility or insolubility in ether it is advisable to test the solubility in benzene and classify the compound into S_1 or S_2 as the result of this test. Commercial ether often contains alcohol, which changes its solvent properties considerably.

Solubility in Dilute Hydrochloric Acid. Aliphatic amines, primary, secondary, and tertiary, form salts (polar compounds) with hydrochloric acid. Hence aliphatic amines are readily soluble in dilute hydrochloric acid.

Aryl groups diminish the basicity of the nitrogen atom; primary aromatic amines, although more weakly basic than primary aliphatic amines, are in Class B; diarylamines and triarylamines are not soluble in dilute hydrochloric acid. Diphenylamine, triphenylamine, and carbazole, for example, are in Class M and not in Class B. Arylalkylamines containing not more than one aryl group are in Class B.

Disubstituted amides ($RCONR_2$) which are of sufficiently high molecular weight to be water insoluble are in Class B, being soluble in dilute hydrochloric acid. This behavior contrasts with that of the simple amides ($RCONH_2$), which are neutral compounds in Class M. Most monosubstituted amides ($RCONHR$) also are neutral and belong in Class M. *N*-Benzylacetamide, however, is in Class B.

It should be noted that amines may react with 5% hydrochloric acid to form insoluble hydrochlorides. Compounds of this type are best classified as soluble. For example, certain arylamines, such as α -naphthylamine, form hydrochlorides which are sparingly soluble in dilute hydrochloric acid. By warming the mixture slightly and diluting it with water, solution sometimes may be effected. The appearance of the solid usually will show whether the amine has undergone a change. In order to decide doubtful cases, the solid should be separated and its melting point compared with that of the original compound. A halogen test with

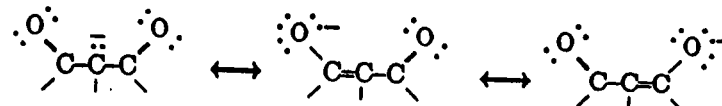
SOLUBILITY IN DILUTE SODIUM HYDROXIDE SOLUTIONS 81

alcoholic silver nitrate would indicate formation of a hydrochloride.

A few types of oxygen-containing compounds that form oxonium salts upon treatment with hydrochloric acid also are in Class B.

Solubility in Dilute Sodium Hydroxide Solutions and in Dilute Solutions of Sodium Bicarbonate. Carboxylic acids, sulfonic acids, sulfinic acids, phenols, some enols, imides, primary and secondary nitro compounds, arylsulfonyl derivatives of primary amines, unsubstituted arylsulfonamides, oximes, thiophenols, and many less familiar types of compounds are soluble in dilute sodium hydroxide solutions. Of these only the three first-mentioned groups are soluble in dilute solutions of sodium bicarbonate.

Aldehydes and ketones are sufficiently acidic to react with aqueous alkali to yield anions which serve as reaction intermediates in such processes as the aldol condensation; they are far too weakly acidic, however, to dissolve to any measurable extent in sodium hydroxide solution. When two carbonyl groups are attached to the same carbon atom as they are in acetoacetic and malonic esters and in 1,3-diketones, the acidity increases sharply because of the added stabilization of the anion in which the negative charge can be distributed on two oxygen atoms as well as the carbon atom.



Dissociation constants that illustrate this point are the following.¹⁴

$CH_3COCH_2COOC_2H_5$	2×10^{-11}
$CH_3COCH(C_2H_5)COOC_2H_5$	2×10^{-13}
$CH_2(COOC_2H_5)_2$	5×10^{-14}
$CH_3COCH_2COCH_3$	1×10^{-9}

It should be noted that, although these substances are approximately as acidic as the phenols, the rate of proton removal from carbon may be a relatively slow reaction¹⁴ and the rate of solution of such substances may be so slow that they appear to be insoluble in base.

¹⁴ See Pearson and Mills, *J. Am. Chem. Soc.*, 72, 1692 (1950).

Even one nitro group confers sufficient acidity on a substance to make it soluble in dilute sodium hydroxide. Thus nitroethane¹⁴ has a K_a of about 3.5×10^{-4} .

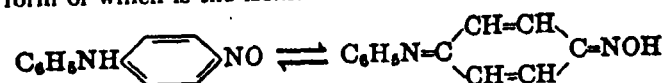
It is of interest that nitro compounds have a tautomeric form, the *aci* form, which is approximately as strong an acid as the carboxylic acids. The *aci* form of nitroethane has a K_a of 3.6×10^{-5} .

Just as the grouping $\begin{array}{c} \text{O} \quad \text{H} \quad \text{O} \\ | \quad | \quad | \\ -\text{C}-\text{C}-\text{C}- \end{array}$ is acidic, so is the imide grouping

$\begin{array}{c} \text{O} \quad \text{H} \quad \text{O} \\ | \quad | \quad | \\ -\text{C}-\text{N}-\text{C}- \end{array}$, and imides belong in general in Class A_2 .

Even a *p*-nitrophenyl group attached to the nitrogen atom is sufficient to make an amide acidic. *p*-Nitroacetanilide is sufficiently acidic to fall in Class A_2 . Only one RSO_2 grouping is required to make sulfonamides (RSO_2NH_2) acidic enough to belong in Class A_2 .

Many compounds carrying a hydroxyl group on a nitrogen atom are sufficiently acidic to be in Class A_2 . Oximes illustrate this type. An interesting example is *p*-nitrosodiphenylamine, the *aci* form of which is the isomeric oxime.



Esters containing five or six carbon atoms that are almost completely soluble in water may be hydrolyzed by continued shaking with dilute sodium hydroxide solution. The alkali should not be heated, and the solubility or insolubility should be recorded after 1 to 2 minutes.

Fatty acids containing twelve or more carbon atoms react with the alkali slowly, forming salts which are soaps. The mixture is not clear but consists of an opalescent colloidal dispersion that foams when shaken. Once this behavior has been observed it is easily recognized. Such acids are placed in Class A_1 .

Certain of the sodium salts of highly substituted phenols are insoluble in sodium hydroxide. This property may be detected by trying the solubility of any residue in water. Certain phenols which are very insoluble in water may precipitate owing to hydrolysis and hence appear to be insoluble in alkali.

¹⁴ See Pearson and Dillon, *J. Am. Chem. Soc.*, 72, 3574 (1950).

Amphoteric Compounds. Compounds containing both an acidic and a basic group are amphoteric. Low-molecular-weight amino acids exist largely as dipolar salts.



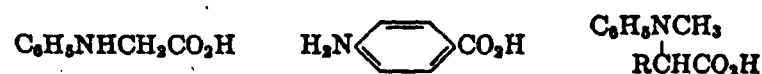
They are soluble in water but not in ether and are in Class S_2 .

The water-insoluble amphoteric compounds are placed in Class $A_1(\text{B})$ or $A_2(\text{B})$, depending on the relative basicity of the amino group, since the basicity determines the extent to which the acidic group will be neutralized by inner salt formation. If the amino group carries only aliphatic substituents, the compounds will dissolve in hydrochloric acid and sodium hydroxide but not in sodium bicarbonate. Compounds of the following types illustrate this group.



They fall in Class $A_2(\text{B})$.

The presence of an aryl group on the nitrogen atom, however, diminishes its basicity so that such compounds fall in Class $A_1(\text{B})$. This is illustrated by the following compounds.



If two aryl groups are attached to the nitrogen atom the compound is not amphoteric and belongs in Class A_1 .



Many other amphoteric compounds in Class $A_2(\text{B})$ are known. These contain basic amino groups as well as the weakly acidic groups characteristic of Class A_2 compounds. Examples are the water-insoluble aminophenols, aminothiophenols, and aminosulfonamides.

Solubility in Syrupy Phosphoric Acid. Alcohols, aldehydes, methyl ketones, cyclic ketones, and esters dissolve in 85% phosphoric acid provided that they contain fewer than nine carbon atoms. For ethers the solubility limit appears to be somewhat lower than this. Thus ethyl ether dissolves in 85% phosphoric

trated sulfuric acid and hence form a distinct layer on top of the acid. Alcohols exhibiting this behavior are considered soluble and placed in Class N_1 or N_2 . Benzyl alcohol and its substitution products dissolve in concentrated sulfuric acid, which causes condensation to form orange-colored insoluble precipitates. Such compounds are classified as soluble and placed in Class N_1 or N_2 .

BORDERLINES BETWEEN SOLUBILITY CLASSES

In Table XII are listed a number of compounds selected in such a way as to show the position of the most important of the various borderlines between solubility classes. These compounds have been grouped as far as possible according to chemical nature. In each group an attempt has been made to include the borderline members together with one or more members at either side of the borderlines. The solubility class of a compound not listed will be evident by considering its relation to the borderline members of the series to which it belongs. Thus the table shows *n*-butyl alcohol to be in Class S_1 ; it follows that the other butyl alcohols and all lower homologs are in this class also. Similarly, since isoamyl alcohol is in Class N_1 it follows that *n*-amyl alcohol and all higher alcohols are in N_1 or N_2 .

TABLE XII

SHOWING THE POSITION OF THE PRINCIPAL BORDERLINES

Compound	Solubility Class	Compound	Solubility Class
Acids		Esters	
Chloroacetic.....	S_1	Ethyl acetate.....	S_1-N_1
<i>n</i> -Butyric.....	S_1	Methyl propionate.....	S_1
α -Chloropropionic.....	S_1	<i>n</i> -Propyl formate.....	S_1
Crotonic.....	S_1	Isopropyl acetate.....	S_1
Isovaleric.....	S_1-A_1	<i>n</i> -Propyl acetate.....	S_1-N_1
Valeric.....	A_1	Methyl isobutyrate.....	S_1-N_1
Alcohols		<i>n</i> -Butyl formate.....	S_1-N_1
<i>n</i> -Butyl.....	S_1	Methyl isovalerate.....	N_1
<i>t</i> -Amyl.....	S_1	<i>sec</i> -Butyl acetate.....	N_1
Isopropylmethylecarbinol..	S_1-N_1	<i>n</i> -Butyl acetate.....	N_1
Isoamyl.....	S_1-N_1	Benzyl acetate.....	N_1
Benzyl.....	N_1	Ethyl caprylate.....	N_2
Cyclopentanol.....	N_1	Ethyl benzoate.....	N_2
Aldehydes		Methyl carbonate.....	S_1-N_1
Isobutyraldehyde.....	S_1	Ethyl oxalate.....	S_1-N_1
<i>n</i> -Butyraldehyde.....	S_1-N_1	Methyl malonate.....	S_1-N_1
Isovaleraldehyde.....	N_1	Ethyl carbonate.....	S_1-N_1
Amides		Ethyl succinate.....	N_1
Formamide.....	S_1-S_2	Ethyl phthalate.....	N_1
Acetamide.....	S_1-S_2	Ethyl malonate.....	N_2
Propionamide.....	S_1-S_2	<i>n</i> -Butyl carbonate.....	N_1-N_2
Isobutyramide.....	S_1-S_2	<i>n</i> -Butyl oxalate.....	N_2
<i>n</i> -Butyramide.....	S_1-M	Ethers	
Formanilide.....	S_1-M	Ethyl methyl.....	S_1
Acetanilide.....	M	Ethyl.....	S_1-N_1
Amines		Ethyl isopropyl.....	S_1-N_1
Diethyl.....	S_1	Isopropyl.....	N_1
Isoamyl.....	S_1	<i>n</i> -Butyl.....	N_2
<i>n</i> -Amyl.....	S_1	Hydrocarbons (aromatic)	
Benzyl.....	S_1	Mesitylene.....	N_2
Piperidine.....	S_1	Isodurene.....	N_2
Cyclohexyl.....	S_1	Cymene.....	I
Di- <i>n</i> -propyl.....	S_1-B	<i>p</i> -Xylene.....	N_2-I
Di- <i>n</i> -butyl.....	B	Diphenylmethane.....	N_2-I
Aniline.....	B	<i>m</i> -Xylene.....	N_2-I
Tri- <i>n</i> -propyl.....	B	<i>o</i> -Xylene.....	N_2-I

with dilute nitric acid and boiled to expel hydrogen cyanide and hydrogen sulfide. Sufficient silver nitrate is added to precipitate completely all the halogens as silver halides, and the precipitate is removed. If both nitrogen and sulfur are present, the precipitate is boiled for 10 minutes with 30 ml. of concentrated nitric acid to destroy any silver thiocyanate that may be present. The mixture is then diluted with 30 ml. of distilled water and filtered. The precipitate of silver halides is then boiled with 20 ml. of 0.1% sodium hydroxide for 2 minutes. The solution is filtered, the filtrate is acidified with nitric acid, and silver nitrate solution is added. A white precipitate indicates chlorine.

(H) *Fluorine*. About 2 ml. of the stock solution is acidified with acetic acid, and the solution is boiled and cooled. One drop of the solution is placed on a piece of zirconium-alizarin test paper. A yellow color on the red paper indicates the presence of fluoride. The test paper is prepared by dipping a piece of filter paper into a solution composed of 3 ml. of 1% ethanolic alizarin solution and 2 ml. of a 0.4% solution of zirconium chloride (or nitrate). The red filter paper is dried and, just before use, is moistened with a drop of 50% acetic acid.

THE SOLUBILITY CLASSES

Three general kinds of information can be obtained about an unknown substance by a study of its solubility behavior in various liquids: namely, water, ether, 5% sodium hydroxide solution, 5% sodium bicarbonate solution, 5% hydrochloric acid, cold concentrated sulfuric acid, and 85% phosphoric acid. First, the presence of a functional group is often indicated. For instance, since hydrocarbons are insoluble in water, the mere fact that an unknown such as ethyl ether is partially soluble in water indicates that a functional group is present. Second, solubility in certain solvents often leads to more specific information about the functional group. For example, benzoic acid is insoluble in the polar solvent, water, but is converted by dilute sodium hydroxide to a salt, sodium benzoate, which is readily water-soluble. In this case, then, the solubility in 5% sodium hydroxide solution of a water-insoluble unknown is a strong indication of an acidic functional group. Finally, certain deductions about molecular weight may sometimes be made. For example, in many homologous series of monofunctional compounds the members with less than about five carbon atoms are water-soluble while the higher homologs are insoluble.

The solubility tests are summarized in Fig. 21. Compounds are divided at the outset into two great groups according to their solubility in water. Each of these groups is then subdivided by the use of the other solvents. The water-soluble compounds are divided into two classes: those soluble in ether (Class S_1) and those insoluble in ether (Class S_2). In considering solubility in inert solvents such as water or ether, a substance is arbitrarily said to be "soluble" if it dissolves to the extent of 3 g. per 100 ml. of solvent. Care should be used in interpreting classifications of "soluble" and "insoluble" in other references since different definitions of the words are often used.

When solubility in dilute acid or base is being considered, it is seen that the significant observation to be made is not whether the unknown is soluble to the extent of 3% or to any arbitrary extent, but, rather, whether it is significantly more soluble in aqueous acid

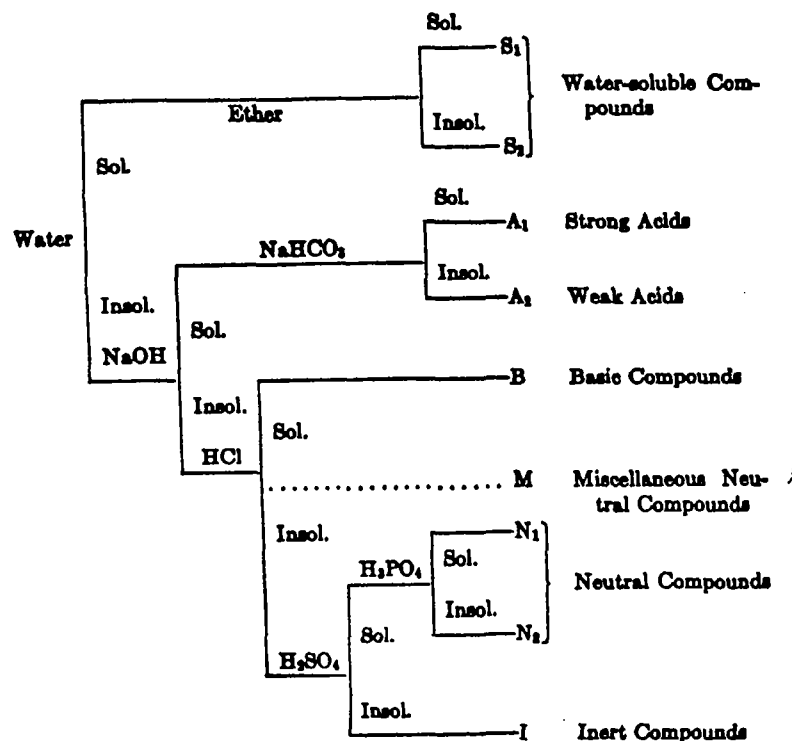


FIG. 21. Division of organic compounds into solubility classes.

or base than it is in water. Such increased solubility is the desired positive test for an acidic or basic functional group.

Acidic compounds are discovered by their solubility in 5% sodium hydroxide. Strong and weak acids (Classes A₁ and A₂, respectively) are differentiated by the solubility of the former but not the latter in the weakly basic solvent, 5% sodium bicarbonate. Basic compounds (Class B) are detected by their solubility in 5% hydrochloric acid, and no attempt is made, in general, to distinguish between strong and weak bases.

Many compounds that are neutral even in strong aqueous acid solutions behave as bases in more acidic solvents such as concentrated sulfuric acid or syrupy phosphoric acid. In general, compounds containing sulfur or nitrogen have an atom with an unshared pair of electrons and would be expected to dissolve in such strongly acidic media. No additional information would be gained therefore by observing such solubility, and for this reason, when the elementary analysis has shown the presence of sulfur or nitrogen, no solubility tests beyond those for acidity and basicity in aqueous solution are carried out. Compounds which contain nitrogen or sulfur and are neutral in aqueous acid or base are placed in solubility Class M.

Most compounds neutral in water and containing oxygen in any form are reasonably strong bases in concentrated sulfuric acid. Solubility in, or any other evidence of a reaction with, this reagent is indicative of an oxygen atom or else of a reactive hydrocarbon function such as an olefinic bond or easily sulfonated aromatic ring; such compounds are said to be in Class N. A further and rather arbitrary distinction is made with syrupy phosphoric acid, Class N₁ compounds being soluble in this reagent as well as in sulfuric acid and Class N₂ compounds being soluble only in the latter. Compounds which are too weakly basic to dissolve in sulfuric acid are placed in Class I.

Since the solubility behavior of water-soluble compounds gives no information about the presence of acidic or basic functional groups, this information must be obtained by testing their aqueous solutions with litmus paper. It might be noted that, in general, the behavior of an acid in 5% hydrochloric acid and of a base in sodium hydroxide solution should be examined routinely since the molecule may have both acidic and basic functional groups (Class A₁-B or A₂-B).

A more detailed survey of the solubility classes is given later (p. 78).

DETERMINATION OF THE SOLUBILITY CLASS

A. Experiment on Known Compounds

Place 0.2 ml. (0.1 g. of a solid) of the compound in a test tube, and add in portions 3 ml. of water. Shake vigorously after the addition of each portion of solvent, being careful to keep the mix-